results of their investigation of the structure of calcium peroxide octahydrate, which is isomorphous with strontium and barium peroxide octahydrate. Their proposed structure of $CaO_2.8H_2O$ is quite similar to that of $Sr(OH)_2.8H_2O$, the main difference being the arrangement of the oxygen ions in the c_0 direction. They have reported that the calculated structure factors based on the square antiprism configuration of water molecules about the positive metal ion gave slightly better agreement with the observed structure factors than those based on the cubic arrangement.

From the above discussion it is concluded that the correct set of strontium positions is the set 0, 0, $\frac{1}{4}$.

The author wishes to express his sincere appreciation to Dr R. E. Rundle for his many helpful discussions during the course of this investigation. He wishes to thank Mr D. S. Gibbs for growing the single crystals of $Sr(OH)_2.8H_2O$ and making a hydrate analysis of the compound, and Mr Marvin Margoshes for supplying the infra-red spectrum of the compound.

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The Crystal Structures of Nickel Acetate, $Ni(CH_3COO)_2.4H_2O$, and Cobalt Acetate, $Co(CH_3COO)_2.4H_2O$

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Crystals of nickel acetate, $Ni(CH_3COO)_2.4H_2O$, are monoclinic with space group $P2_1/c$. The unit cell, of dimensions $a = 4{\cdot}75$, $b = 11{\cdot}77$, $c = 8{\cdot}44$ Å, $\beta = 93° 36'$, contains two formula units. Projections of the structure on two crystallographic planes are given.

The unit cell dimensions of cobalt acetate, $Co(CH_3COO)_2.4H_2O$, are $a = 4{\cdot}77$, $b = 11{\cdot}85$, $c = 8{\cdot}42$ Å, $\beta = 94° 30'$. The space group is $P2_1/c$, and the unit cell contains two formula units. By analogy it is shown that the two compounds are isostructural.

In both cases the metal atoms are surrounded octahedrally by four water molecules and by two oxygen atoms which belong to two different acetate groups. It is shown that these octahedral bonds are probably ionic in character. In the structure the individual formula units are firmly linked by a three-dimensional network of hydrogen bonds.

Introduction

In three earlier communications the authors (van Niekerk & Schoening, 1953*a*, *b*; van Niekerk, Schoening & de Wet, 1953) have reported the existence of direct metal-to-metal bonds in the structures of cupric and chromous acetate. The unusual structural features of these two compounds have led to a systematic X-ray examination of the acetates of other transition elements of which the present investigation forms the first part. Although only the structure of nickel acetate is described in detail in this paper, it is shown that nickel and cobalt acetate are in fact isostructural so that the interatomic distances given for the former also apply to corresponding distances for the latter.

Crystal data

Crystals of nickel acetate, $Ni(CH_3COO)_2.4H_2O$, are monoclinic and emerald green in colour. The unit-cell dimensions, as determined from rotation and Weissenberg photographs, are:

a (Å)	b (Å)	c (Å)	β
4·75	11·77	8·44	93° 36′

These are in good agreement with the values $a = 4{\cdot}75$, $b = 11{\cdot}75$, $c = 8{\cdot}46$ Å and $\beta = 93° 34'$ previously obtained by Hull (1938).

Systematic extinctions occur for $h0l$ with l odd and for $0k0$ with k odd. The space group is therefore $P2_1/c$. The number of formula units (Z) in the unit cell is two.

The calculated density $D_x = 1·75$ g.cm.$^{-3}$ agrees with the measured density $D_m = 1·79$ g.cm.$^{-3}$.

For cobalt acetate, $Co(CH_3COO)_2.4H_2O$, which has been reported to be isomorphous with nickel acetate (Rammelsberg, 1853), the corresponding data are:

a (Å)	b (Å)	c (Å)	β
4·77	11·85	8·42	94° 30′

$P2_1/c$, $Z = 2$, $D_x = 1·74$ g.cm.$^{-3}$ and $D_m = 1·704$ g.cm.$^{-3}$. The axial ratios $a:b:c = 0·4025:1:0·7105$ agree with the values $a:b:c = 0·7196:1:0·4030$, $\beta = 94° 41'$ given by Rammelsberg.

Determination of the structure

For evaluating the $\sigma(x, z)$ and $\sigma(y, z)$ projections of nickel acetate the relevant spectra were recorded on zero-layer Weissenberg photographs using the multiple-film technique. Filtered Mo $K\alpha$ radiation was used. The intensities of the reflexions were estimated visually and corrected for Lorentz and polarization factors in the usual way. In view of the small size of the crystals used no corrections were made for absorption and extinction.

Because the general point position in the $P2_1/c$ space group is fourfold, and since the unit cell contains only two formula units, it follows that the nickel atoms must lie on symmetry centres. Using as origin that given in *International Tables* for the $P2_1/c$ space group, the nickel position was taken at (0, 0, 0).

The $\sigma(y, z)$ projection was evaluated first as it promised the clearest resolution. For this purpose the signs of the $F(0kl)$ values were calculated on the assumption that they were determined by the nickel atom only. It may be noted that during the preliminary stages only those values of $F(0kl)$ for which $k+l$ is even could be used as the nickel atom does not contribute towards spectra for which $k+l$ is odd. Successive refinements, including all the observed spectra, gave the final $\sigma(y, z)$ projection shown in Fig. 1.

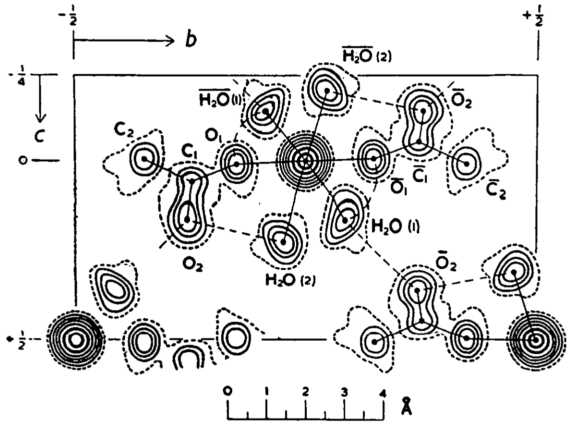

Fig. 1. $\sigma(y, z)$ projection. Contours are drawn at intervals of 2 e.Å^{-2}. The broken contour is the 2 e.Å^{-2} level. The heavy lines of the Ni peak represent the 30 and 50 e.Å^{-2} levels.

In a similar manner the nickel acetate structure was also projected on the $a\,c$ plane and the final $\sigma(x, z)$ projection is shown in Fig. 2.

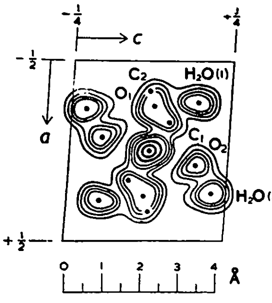

Fig. 2. $\sigma(x, z)$ projection. Contours are drawn as for Fig. 1, the outer contour being the 4 e.Å^{-2} level.

The co-ordinates, which were estimated from the two projections, are given in Table 1.

With these co-ordinates, structure factors were calculated using the following temperature corrections: for the nickel atom an isotropic temperature factor with $B = 1·4$ was used, for the carbon atoms the f values given by Robertson (1935) were used while the f values of the oxygen atoms were reduced proportionately. In Table 2 the observed (F_o(Ni)) and the calculated (F_c) structure factors for nickel acetate are given. The agreement is excellent and leads to R factors of 0·13 and 0·18 for $F(0kl)$ and $F(h0l)$ respectively, not taking absent spectra into account.

Table 1. *Final parameters*

	x	y	z
Ni	0·000	0·000	0·000
O_1	−0·247	−0·150	0·008
O_2	0·075	−0·258	0·150
$H_2O(1)$	−0·273	0·087	0·147
$H_2O(2)$	0·233	−0·050	0·203
C_1	−0·158	−0·247	0·060
C_2	−0·333	−0·350	−0·007

The interatomic distances and the angles tabulated in Table 3 were calculated from the atomic co-ordinates given under Table 1.

In Table 2 is also given a set of observed structure factors (F_o(Co)) for cobalt acetate, $Co(CH_3COO)_2.4H_2O$, which were obtained in a manner exactly similar to that described for nickel acetate. By comparing these F_o(Co) values with the corresponding F_c values of nickel acetate, and disregarding absent spectra, R factors of 0·14 and 0·19 were obtained for the $0kl$ and $h0l$ spectra respectively. Considering this agreement together with the similarity of the unit-cell dimensions of cobalt and nickel acetate, it is concluded that, within the errors of experiment, the two compounds are isostructural and that the distances and angles given in Table 3 also give the corresponding values for the cobalt acetate structure.

Table 2

hkl	F_c	F_o (Ni)	F_o (Co)
000			
100	+72	62	61
200	−17	20	22
300	+40	30	28
400	+32	45	41
500	+13	16	9
600	+9	< 8	—
700	+8	10	10
020	+25	26	25
040	+42	36	42
060	+11	14	13
080	+37	41	38
0,10,0	−3	< 7	—
0,12,0	+27	33	35
0,14,0	+13	13	10
0,16,0	+10	12	—
002	+64	47	53
004	+40	40	38
006	+52	50	47
008	+24	21	19
0,0,10	+14	12	10
011	+80	56	54
012	+27	25	23
013	+16	9	9
014	0	< 5	—
015	+43	44	42
016	+6	9	10
017	+23	22	20
018	+2	< 8	—
019	+17	15	13
0,1,10	−1	< 9	—
0,1,11	+11	10	—
021	−3	< 3	—
022	+13	8	8
023	−10	11	11
024	+37	36	39
025	+16	15	16
026	+30	22	21
027	+4	< 7	—
028	+17	16	17
029	−2	< 9	—
0,2,10	+17	16	14
031	+40	40	41
032	−38	38	42
033	+21	18	21
034	−2	< 6	—
035	+31	30	30
036	+13	14	13
037	+15	18	16
038	−11	8	11
039	+16	15	16
0,3,10	+1	< 10	—
041	+8	5	5
042	+16	11	9
043	−15	16	20
044	+13	14	15
045	+4	< 7	—
046	+14	16	17
047	0	< 8	—
048	+8	< 8	—
049	−6	< 9	—
051	+26	28	23
052	+22	23	25
053	+47	46	45
054	−9	8	11
055	+26	24	28
056	+7	7	8
057	+14	10	9
058	−1	< 9	—
059	+16	13	10
0,5,10	−1	< 10	—
0,5,11	+20	11	—
061	+11	11	15
062	+53	50	54
063	−8	11	8
064	+52	56	51
065	+1	< 7	—
066	+22	21	22
067	0	< 8	—
068	+22	23	19
069	−4	< 9	—
0,6,10	+19	20	15
071	+29	29	27
072	−2	< 6	—
073	+38	42	38
074	−9	9	—
075	+21	21	22
076	+2	< 8	—
077	+19	17	20
078	−3	< 9	—
079	+13	16	13
081	+19	16	16
082	+38	43	35
083	+2	< 7	—
084	+21	23	21
085	−5	< 8	—
086	+20	19	15
087	+4	< 9	—
088	+15	16	10
089	+3	< 10	—
091	+20	23	25
092	+18	22	24
093	+27	31	31
094	−3	< 8	—
095	+13	14	12
096	−1	< 9	—
097	+20	13	14
098	+4	< 10	—
099	+11	10	11
0,10,1	+1	< 7	—
0,10,2	+13	15	10
0,10,3	+1	< 8	—
0,10,4	+9	< 8	—
0,10,5	0	< 9	—
0,10,6	+11	< 9	—
0,10,7	0	< 9	—
0,10,8	+12	12	15
0,11,1	+21	20	15
0,11,2	−6	< 8	—
0,11,3	+14	16	13
0,11,4	−1	< 9	—
0,11,5	+12	9	—
0,11,6	−2	< 10	—
0,11,7	+18	22	18
0,11,8	−1	< 10	—
0,12,1	−2	< 8	—
0,12,2	+21	24	24
0,12,3	0	< 9	—
0,12,4	+12	9	10
0,12,5	−3	< 10	—
0,12,6	+16	17	15
0,13,1	+16	20	16
0,13,2	0	< 9	—
0,13,3	+16	16	12
0,13,4	+4	< 10	—
0,13,5	+11	10	10
0,14,1	−5	< 9	—
0,14,2	+17	21	17
0,14,3	+1	< 10	—
0,14,4	+16	17	15
0,14,5	+4	< 10	—
0,14,6	+12	15	14
0,15,1	+12	14	11
102	+42	47	44
104	+39	50	48
106	+19	20	20
108	+20	24	20
1,0,10	+9	< 9	12
$10\bar{2}$	+26	33	23
$10\bar{4}$	+4	5	—
$10\bar{6}$	+34	31	31
$10\bar{8}$	+10	< 8	—
$1,0,\overline{10}$	+11	< 9	—
202	+15	15	15
204	+29	29	27
206	+19	19	19
208	+12	11	—
$20\bar{2}$	+39	42	35
$20\bar{4}$	−2	< 7	—
$20\bar{6}$	+4	< 7	—
$20\bar{8}$	+17	14	12
$2,0,\overline{10}$	+10	< 9	—
302	+16	14	12
304	+25	22	21
306	+34	39	36
308	+12	9	—
$30\bar{2}$	+43	38	32
$30\bar{4}$	+23	18	16
$30\bar{6}$	+18	10	15
$30\bar{8}$	+26	26	24
402	+14	22	17
404	+16	24	25
406	+19	28	26
408	+11	9	12
4,0,10	+10	10	—
$40\bar{2}$	+21	23	21
$40\bar{4}$	+26	29	28
$40\bar{6}$	+22	28	30
$40\bar{8}$	+17	18	13
502	+12	14	15
504	+15	27	25
506	+6	< 10	—
508	+8	< 11	—
$50\bar{2}$	+19	24	21
$50\bar{4}$	+17	20	18
$50\bar{6}$	+12	18	14
602	+12	11	10
604	+13	17	13
$60\bar{2}$	+18	23	20
$60\bar{4}$	+11	9	12
702	+9	10	—

Table 3. *Bond lengths and angles*

Ni–O_1	2·12 Å	O_1–O_2	2·27 Å
Ni–$H_2O(1)$	2·11	O_1–C_1	1·29
Ni–$H_2O(2)$	2·06	O_2–C_1	1·31
		C_1–C_2	1·56

O_1–Ni–$H_2O(1)$	90° 44′
O_1–Ni–$H_2O(2)$	90° 33′
$H_2O(1)$–Ni–$H_2O(2)$	88° 30′
O_1–C_1–O_2	121° 39′

Description of the structure

The structure is best described by referring to Fig. 1. Each nickel atom is surrounded octahedrally by four water molecules ($H_2O(1)$, $H_2O(2)$, $\overline{H_2O}(1)$ and $\overline{H_2O}(2)$) and by two oxygen atoms (O_1 and $\overline{O}_1$), the latter two atoms belonging to two different acetate groups. The remaining oxygen atom (O_2 or $\overline{O}_2$) of an acetate group is linked by a hydrogen bond of length 2·59 Å to a water molecule ($H_2O(2)$ or $\overline{H_2O}(2)$) within the same nickel co-ordination group. These bonds are indicated in the diagram by broken lines.

The two acetate groups and the four water molecules which constitute the nearest neighbours of a nickel atom at (0, 0, 0) are further linked by hydrogen bonds to similar groups surrounding the nickel atoms at (½, 0, 0) and at (0, ½, ½). The way in which this is accomplished is as follows: the water molecule $H_2O(1)$ belonging to the (0, 0, 0) group makes one hydrogen bond (2·66 Å) to the $\overline{O}_1$ oxygen atom of the group at (½, 0, 0) and also a second hydrogen bond of length 2·64 Å to the oxygen atom $\overline{O}_2$ belonging to the group at (0, ½, ½). In the diagram such bonds are indicated by broken arcs and by broken lines respectively.

Within the errors of experiment the acetate groups are found to be separately planar. The O_1–C_1 and O_2–C_1 distances are 1·29 and 1·31 Å respectively and the C_1–C_2 distance is 1·56 Å.

Discussion of the bonding

The bond distances between the nickel atom and the four water molecules (2·11 and 2·06 Å) and between the nickel atom and the two oxygen atoms (2·12 Å) in the nickel acetate structure can be compared with similar distances in other octahedrally co-ordinated nickel structures. Thus in $NiSO_4.6H_2O$ the nickel–water distances are 2·02 and 2·04 Å and in $NiSO_4.7H_2O$ they vary between 1·95 and 2·13 Å (Wyckoff, 1951). As is the case in other hydrated nickel salts, the nickel–water and nickel–oxygen bonds in this structure are probably mainly ionic in character.

In cobalt acetate the cobalt–water (2·11 and 2·06 Å) and cobalt–oxygen (2·12 Å) distances seem to indicate essentially ionic bonds, as will be seen when comparing these distances with the calculated 1·98 Å covalent bond length and the calculated 2·12 Å ionic bond length for cobalt structures. The instability of 6-covalent cobaltous compounds further supports the conclusion that the bonds discussed above are probably ionic in character.

Whereas the co-ordinates of the oxygen atoms are sufficiently accurate to permit the evaluation of reliable bond distances, those of the carbon atoms, particularly those of C_1, are not very reliable, so that the approximate equality of the two C–O bonds (1·29 and 1·31 Å) in an acetate group may or may not be real. However, should these distances be equal, as the calculations suggest, it could be explained by the surrounding of the oxygen atoms in the following way: one oxygen atom of an acetate group is linked by two hydrogen bonds to two water molecules, while the other oxygen atom makes one hydrogen bond to a water molecule and also an ionic bond to the doubly positive metal ion. The influence of these bonds on the two oxygen atoms of an acetate group may be equal, thus accounting for the equal lengths of the oxygen–carbon bonds.

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